AD-A225 363

OFFICE OF NAVAL RESEARCH

Contract N00014-84-G-0201

Task No. 0051-865

Technical Report #34

The Synthesis of Monometallated and Unsymmetrically Substituted Binuclear
Phthalocyanines and a Pentanuclear Phthalocyanine
by Solution and Polymer Support Methods

By

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in

Journal of Organic Chemistry

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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION	1b RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION / AVAILABILITY OF REPORT
Unclassified	As it appears on the report
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
Report # 34	

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
A.B.P. Lever, York University Chemistry Department		Office of Naval Research

6c. ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
4700 Keele St., North York, Ontario M3J 1P3 Canada	Chemistry Division 800 N. Quincy Street Arlington, VA 22217 U.S.A.

8a. NAME OF FUNDING / SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
		N00014-84-G-0201

8c. ADDRESS (City, State, and ZIP Code)	10 SOURCE OF FUNDING NUMBERS			
	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO	WORK UNIT ACCESSION NO

11. TITLE (Include Security Classification)

The Synthesis of Monometallated and Unsymmetrically Substituted Binuclear Phthalocyanines and a Pentanuclear Phthalocyanine by Solution and Polymer Support Methods

12 PERSONAL AUTHOR(S)
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13a. TYPE OF REPORT	13b. TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical	FROM Aug. '89 TO Aug.'90	August 3, 1990	43

16. SUPPLEMENTARY NOTATION

17	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Phthalocyanine, Binuclear, Pentanuclear, Polymer Support

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

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20 DISTRIBUTION / AVAILABILITY OF ABSTRACT	21 ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	Unclassified/unlimited
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b TELEPHONE (Include Area Code)	22c OFFICE SYMBOL
Dr. Ronald A. De Marco		

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted
All other editions are obsolete

TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

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THE SYNTHESES OF MONOMETALLATED AND UNSYMMETRICALLY SUBSTITUTED BINUCLEAR PHTHALOCYANINES AND A PENTANUCLEAR PHTHALOCYANINE BY SOLUTION AND POLYMER SUPPORT METHODS

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Abstract

Binuclear phthalocyanines in which two different phthalocyanine nuclei are covalently linked through five-atom bridges, derived from 2-ethyl-2-methylpropan-1,3-diol are prepared. In the examples, one phthalocyanine ring is always substituted with neopentoxy substitutents, while the other phthalocyanine ring is unsubstituted or contains a tert-butyl substituents or a neopentoxysubstituted copper phthalocyanine, constituting a binuclear phthalocyanine in which only one ring is metallated. The precursor, 2-(2-hydroxymethyl-2-methylbutoxy)-9,16,23-trineopentoxyphthalocyanine[41] was prepared in solution and also by solid phase methods, using polymer-bound trityl chloride derived from a 1% divinylbenzene-co-styrene co-polymer. A metal-free pentanuclear phthalocyanine, in which four phthalocyaninyl groups are covalently bound to the four benzo groups of a central phthalocyanine nucleus is described and characterized by FAB mass spectroscopy. In some experiments some rare examples of demetallation of some zinc phthalocyanines are noted during phthalocyanine formation. A modified flash chromatography procedure proved to be useful for separating similarly substituted mononuclear phthalocyanines.

Using face-to-face porphyrin dimers, held together by a pair of
covalent amide bridges[1,2] or by a single rigid aromatic bridge[3,4], the four-
electron reduction of dioxygen to water, without forming free hydrogen
peroxide, has been achieved. In most examples, it was the <u>dicobalt</u> por-
phyrin dimers that were the active catalysts but Collman et al[5] have shown
that a mixed metal <u>cobalt-silver</u> cofacial porphyrin dimer could also promote
a four-electron reduction of O_2.

As the porphyrin dimer catalysts tend to decompose after several
cycles, we have been attempting to find similar catalysts that would be more
stable under similar conditions. To this end we have prepared, for the
first time, a whole series of binuclear phthalocyanines[6,7,8], covalently
linked by 5, 4, 3, 2, 1, 0 and "-1" bridges and a unique tetranuclear
phthalocyanine[9]. To date, however, none of the multinuclear phthalocyanines
have achieved the desired four-electron of O_2, although the two-electron
reduction of many of the multinuclear phthalocyanines have been more
efficient[9,10] relative to simple mononuclear phthalocyanines. Perhaps, this
fact is not too surprising as only a very few of the porphyrin dimers
prepared by Collman's group[1,2] were good catalysts and it is difficult to
predict the exact co-facial geometry, necessary for a four-electron reduc-
tion, beyond saying that the metal centers of the two macrocycles should be
between 3.5 and 5.0 A. As mixed metal and other unsymmetrically substituted
binuclear phthalocyanines had not previously been prepared, we wished to
examine their synthesis towards the goal of suggesting to us a suitable
geometry for achieving a four-electron reduction of O_2 by stable phthalo-
cyanines. In addition, all previous binuclear phthalocyanines had bulky
neopentoxy substituents and we believed that the bulky groups were prevent-

ing the two phthalocyanine rings from achieving complete cofaciality. We
felt that it might be possible to prepare a binuclear phthalocyanine
containing only one ring having bulky neopentoxy[41] groups, while the other
ring was unsubstituted except for the bridge, and that the one ring contain-
ing bulky groups would be sufficient to enable the binuclear phthalocyanine
to be soluble enough for isolation and purification. Although most por-
phyrin mixed metal dimers are most easily made by cyclization of two
separate porphyrin monomers containing different metals,[1,11] other methods
include a cyclization procedure yielding a mixture of separable porphyrin
dimers[12] and an interesting example in which a silver porphyrin is used as a
protecting group in the synthesis of mixed metal porphyrin dimers[5]. Like
porphyrin dimers can be separated by chromatography[12], but the more highly
aggregating[9,13] phthalocyanines would be difficult to separate by this
method. Binuclear phthalocyanines are prepared by the simultaneous forma-
tion of the two phthalocyanine rings from a bridged bisphthalonitrile[8] and
hence methods similar to those used in porphryin chemistry[14] are not yet ap-
plicable and, lastly, the formation of phthalocyanines[15] occurs at higher
temperatures (150 $^\circ$C) than porphyrins so that the likelihood of transmetal-
lation is high and, as shown below, this complication did arise.

Results and Discussion

Our strategy for the synthesis of binuclear phthalocyanines, containing
differently substituted phthalocyanine rings, was based on some of our
earlier work[16] in which very rare unsymmetrical mononuclear phthalocyanines,
containing one unique "handle" or functionally active substituent was
prepared using polymer-bound trityl chloride as a supporting blocking
group[17]. In this way, first one phthalocyanine ring containing one group of

substituents or metal can be prepared followed by the stepwise elaboration of the second phthalocyanine nucleus containing no metal or different substituents.

Preparation of Mononuclear Phthalocyanines.

Thus, treatment of 4-nitrophthalonitrile (1)[16] with excess 2-ethyl-2-methylpropan-1,3-diol (2) and base gave the desired hydroxy ether 3 and some bis ether 4[7]. The alcohol of hydroxy ether 3 was protected using trityl chloride (5) in pyridine[19] or polymer-supported trityl chloride(6)[17] and 4-dimethylaminopyridine as catalyst[20] to give 7 and 8 respectively (Scheme I). The protected phthalonitriles 7 and 8 and the unprotected phthalonitrile 3 were converted[20,22] to their respective diiminoisoindolines 9-11. Self condensation of 9 or 11 in 2-N,N-dimethylaminoethanol under standard conditions[6,21] gave the tetratrityloxyphthalocyanine 12 and the tetra-hydroxyphthalocyanine 13 respectively. Furthermore, the protecting trityl groups of 12 could be removed under very mild conditions with trimethylsilyl iodide[23] giving the free phthalonitrile 3 and the tetrahydroxyphthalocyanine 13 respectively. This cleavage procedure does not cleave neopentoxy groups and is thus compatible with the planned synthesis of unsymmetrical bi-nuclear phthalocyanines described below (Scheme 1). Treatment of 13 with zinc acetate in toluene gave the tetrahydroxy zinc derivative 14. Compound 14 was recently tested[24] for its efficiency as a possible candidate for use in photodynamic therapy but its synthesis is described herein for the first time.

Condensation of the insoluble polymer-bound bisdiiminoisoindoline 10 with a large excess of 5-neopentoxy-1,3-bisdiiminoisoindoline (15)[6] (derived from 4-neopentoxyphthalonitrile[6,25]) as previously described[16] gave the

unsymmetrically substituted polymer-bound phthalocyanine **16** and the sym-
metrical 2,9,16,23-tetraneopentoxyphthalocyanine[41] (**17**), formed by self-
condensation of **15**. Filtration and Soxhlet extraction of polymer **16** removed
all of **17** from **16**. Cleavage of **16** with trimethylsily iodide as for **8** and **12**
yielded the desired monohydroxytrineopentoxyphthalocyanine[41] **18** in 18%
yield. Metal free **18** was readily converted into its zinc (II) derivative **19**
with zinc acetate in toluene. In addition, the cleavage of **16** gave, after
very extensive chromatographic separations (see Experimental) **18**, and di-
hydroxydineopentoxyphthalocyanines **20** and **21** as a mixture of inseparable
isomers which can be designated as the "adjacent" isomers **20** and the
"opposite" isomers **21** using a terminology recently proposed for similar
isomers in the porphyrin series[26]. As a comparison, condensation of **11** and
excess **15** as before in a homogeneous solution gave a more complex mixture of
substituted phthalocyanines. In another experiment **10** condensed with a
small excess of **15** to see if the polymer-bound isoindoline would self-
condense. In fact, substantial self-condensation did occur. Extensive
chromatographic separation procedures not only gave pure samples of **17**, **18**,
20 and **21**, isolated from the polymer supported experiment using a large
excess of **15** above, but also small samples of a trihydroxyneopentoxyph-
thalocyanine **22** and even the symmetrical tetrahydroxyphthalocyanine **13**,
prepared from the polymer supported experiment using a small excess of **15**.
As envisioned the polymer-bound reaction was cleaner giving fewer condensa-
tion products than a similar solution condensation, but the formation of **20**
and **21** still shows that even on a polymer support conformational mobility is
sufficiently high that two, and even more polymer-bound groups can par-
ticipate in the condensation, depending on the reaction conditions.

Chromatographic Separation of Different Mononuclear Phthalocyanines.

In general, the separation of different substituted mononuclear phthalocyanines from each other by any method including extensive chromatography is difficult[27], although a few successful examples have been reported[27-30]. It is believed that aggregation phenomena inhibit clean separations and even single spots on thin layer chromatography (TLC) can actually be mixtures of compounds. Examination of these fractions by mass spectroscopy has in some cases delineated possible contamination by other phthalocyanine compounds[27]. Since mononuclear phthalocyanines **13**, **17**, **18**, **20** and **21**, and **22**, all contain different numbers of hydroxy groups it was felt that chromatographic separation of <u>this</u> mixture produced in the mixed condensation of **11** and **15** might be possible. We have previously found[16] that vacuum liquid chromatography[31] was a powerful tool for the chromatogrphic separation of very similar compounds including phthalocyanines but the procedure was tedious and elution times slow. We slightly changed the flash chromatography procedure of Still et al[32] in a manner similar to, but not identical with, Taber's modification[33] in packing the columns used for flash chromatography. Mainly, the columns are packed with flash chromatography grade silica (20-45 μm) <u>under vacuum</u> for several minutes (see Experimental). Under these conditions, separations of organic compounds approached the resolution of vacuum liquid chromatography but at elution rates of flash chromatography. Each fraction isolated was analyzed by mass spectroscopy so that pure samples of **13**, **17**, **18**, **20** and **21**, and **22** could be obtained and mixed fractions could be rechromatographed. It should be noted that the possible "adjacent" and "opposite" isomers **20** and **21** could not be separated and characterization rests solely on mass spectroscopy and elemental analy-

sis. Each one of **13**, **17**, **18** and **20-22** itself exists as a mixture of very

closely related regioisomers[34] which in all cases show up as one spot on

TLC. For compound **18**, however, we noted that silica TLC of pure **18** on most

TLC plates exhibited one spot, but on some brands (Eastman Kodak) three very

closely distinct bands developed and were separated by preparative TLC.

Mass spectroscopy of all three bands gave identical spectra consistent with

structure **18**. Compound **18** could exist as a mixture of eight closely related

regiomers and it is possible that these distributed themselves into three

fractions. Examination of each of these bands and also of the **20** and **21**

mixture by nmr spectroscopy, did not aid us in identifying specific isomers

of **20** and **21** or of any regiomers of **13**, **17**, **18** and **22**.

Preparation of Unsymmetrical Binuclear Phthalocyanines.

The synthesis of the monohydroxy substituted phthalocyanines **18** and **19**

allowed us to proceed with the syntheses of the unsymmetrically substituted

binuclear phthalocyanines by the following route (Scheme II). Treatment of

a mixture of **1** and **18** with potassium carbonate in dimethylformanide (DMF)

for five days at room temperature led to a metal-free monophthalonitrilo

substituted phthalocyanine **23**. Me al insertion of zinc and copper into

metal-free **23** was readily achieved by heating **23** with zinc and copper

acetate to give zinc and copper phthalocyanines **24** and **25** respectively.

Conversion of the monophthalonitrilo substituted phthalocyanines **23-25** into

their diiminoisoindolino phthalocyanines **26-28** respectively was accomplished

as for **9-11** above except that dioxane or tetrahydrofuran was required as a

co-solvent to effect solubilization of the poorly soluble **23-25** in methanol.

The key mixed condensation reactions of **26** with a large excess of the simple

diiminoisoindolines **29** and **30**, derived from 4-tert-butylphthalonitrile and

phthalonitrile respectively, under standard conditions for binuclear

phthalocyanine formation gave the unsymmetrical binuclear phthalocyanines **31**

and **32**, respectively, along with the simple mononuclear phthalocyanines **33**

and **34**, derived from self-condensation of **29** and **30**. The preparation of

binuclear phthalocyanine **31** proceded smoothly as expected as both neopentoxy

and tert-butyl groups are bulky and facilitate solubilization of phthalo-

cyanines. Binuclear phthalocyanine **32** was predictably less soluble due to

the lack of substituents on one ring and this fact led to losses in the

purification steps so that the ultimate isolated yield of pure **32** was only

1.8%. The uv-vis spectrum of binuclear **32** was surprising and appeared

similar to metal-free mononuclear phthalocyanines. These data indicate to

us that **32** does not have a cofacial conformation at all and exhibits the

characteristics of two phthalocyanine rings separated by an infinitely long

chain. It thus appears that the bulky neopentoxy, tert-butyl and other

groups actually promote cofacial conformations. Our recent synthesis of a

binuclear phthalocyanine, containing two phthalocyanine rings having no

substituents, except for a very bulky group in the bridge affording solu-

bility, shows a simliar lack of cofacial behaviour[35].

The reactions of the zinc phthalocyanine **27** or the copper phthalo-

cyanine **28** with an excess of the diiminoisoindoline **15** in mixed condensa-

tions led in the former case to a as previously described[6] symmetrical

binuclear phthalocyanine **35** devoid of zinc as determined by FAB mass

spectroscopy, but gave the desired monocopper binuclear phthalocyanine **37**,

in the latter example. Careful examination of the mononuclear phthalo-

cyanine fractions produced in these reactions, exhibited the expected

formation of metal-fee **17**, from self-condensation of **15**, but some 2,9,16,23-

tetraneopentoxy phthalocyaninatozinc(II) (36) was also detected by FAB mass spectroscopy for the reaction with 27. Transmetallation from 27 to 36 through unknown pathways had obviously occurred[36].

Preparation of a Pentanuclear Phthalocyanine.

When the tetrahydroxyphthalocyanine 13 was mixed with excess 4-nitrophthalonitrile 1 and K_2CO_3 in DMF for seven days, all four hydroxy groups displaced the nitro group of 1 to afford the metal-free tetraphthalonitrilophthalocyanine 41 in 87% yield. Treatment of 41 with zinc or copper salts led to the zinc and copper phthalocyanines 42 and 43 respectively. Compounds 41-43 were readily converted to their respective tetradiiminoisoindolines 44-46. Condensation of 41 with an excess of 15 led to the first known pentanuclear phthalocyanine 47 in 12% yield, although pentanuclear porphyrins[37] and a mixed tetraporphyrinylphthalocyanine[38] have been recently described.

<center>Scheme IV</center>

An attempt to make the pentanuclear phthalocyanine in which the core phthalocyanine ring contained zinc and the peripheral phthalocyanine rings were metal-free gave metal-free 47. Again zinc demetallation occurred under the condensation reaction conditions[36].

Spectroscopic Properties of the Phthalocyanines.

The infrared, NMR and FAB mass spectra were consistent with the structures of the binuclear and multinuclear phthalocyanines previously described[7,8]. The ultraviolet-visible (uv-vis) spectrum of 37 shows two prominent peaks in the Q-band region (see expt.) typical of an aggregated (cofacial and intramolecular),[39] dimetallated binuclear phthalocyanine, and indicative of close contact between the copper and metal-free halves of the

molecule. The only evidence of the presumed lower symmetry of this species is a weak shoulder near 704 nm.

Metal free phthalocyanines fluoresce strongly from the Q band.[15] Relative to mononuclear species **17**, under the same concentration conditions (ca 2 x 10^{-6} M in toluene/ethanol (3:2 v/v), and corrected for inner filter effects, the binuclear metal-free species **35** emits at essentially the same wavelength (709 nm) but with some 10% of the intensity of the mononuclear species. Evidently there is significant intramolecular quenching. Copper phthalocyanines are not expected to emit due to the presence of low lying d states. The monocopper species **37** does in fact emit (at 703 nm) with a corrected intensity approximately one half that of the binuclear metal-free species **35**. One might conclude that the emission from the metal-free half of the molecule is largely but not totally quenched by the copper half. However it is possible that total quenching is occurring in cofacial conformers and that the emission comes from a very small concentration of open, non-aggregated conformers, which do not show up in the absorption spectrum.

Conclusion

The synthesis of the monohydroxymethyl substituted phthalocyanines **18** and **19** by solution and solid phase methods and their separation from by-products **20-22** by a modified flash chromatographic procedure has allowed us to prepare, via **18** binuclear phthalocyanines in which each phthalocyanine ring has different substituents and in one example one metal and no metal. Fluorescence spectroscopy showed this latter compound (**37**) was largely but not completely quenched by the lone copper atom. The first known pentanuclear phthalocyanine **47** was prepared and characterized.

Experimental Section

General Methods.

Matheson high purity argon was used to maintain inert atmosphere conditions. Infrared (IR) spectra were recorded on a Pye Unicam SP1000 infrared spectrophotometer using KBr discs for solids or as neat films between NaCl discs. Nuclear magnetic resonance (NMR) spectra for carbons and protons were recorded on a Bruker AM300 NMR spectrometer using deutero-chloroform as a solvent and tetramethylsilane as the internal standard unless otherwise stated. The ^{1}H NMR spectra of the phthalocyanines were obtained by averaging 500-3000 scans over the absorption range while ^{13}C NMR spectra on saturated solutions of phthalocyanines were obtained by averaging 5000-15,000 scans over the absorption range. The positions of the signals are reported in δ units. (The splittings of the signals are described as singlets (s), doublets (d), triplets (t), quartets (q), or multiplets (m).) The visible-ultraviolet spectra (UV) were recorded on a Hewlett Packard HP8451A Diode Array spectrophotometer. Fluorescence spectra were recorded using a Varian SF 330 spectrofluorimeter. Mass spectra (MS) were recorded at 70 eV on a VG Micomass 16F mass spectrometer in the EI mode. The FAB spectra were obtained with a Kratos MS-50 triple analyzer mass spectrometer equipped with a FAB ion source of standard Kratos design and Ion Tech atom gun. The sample was dissolved in chloroform and a microlitre of the resulting solution added to a microlitre of m-nitrobenzyl alcohol on the probe tip. The spectra of the molecular ions of the binuclear phthalocyanines were obtained by signal averaging up to 256 scans over the appropriate mass range. The number in parentheses after the indicataed ion shows the percentage of the base peak represented by that ion. Melting

points (mp) were determined using a Kofler hot stage melting point apparatus
and are uncorrected. Thin-layer chromatography (TLC) was performed using
silica gel G as the absorbent. Flash chromatography was performed using
silica gel of particule size 20-45 μ.m. All reactions were stirred with a
magentic stirrer. All solvents were freshly distilled before use. Micro-
analyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ont.

4-(2-Hydroxymethyl-2-methylbutoxy)benzene-1,2-bicarbonitrile (3).

[4-(2-Hydroxymethyl-2-methylbutoxy)phthalonitrile]. To a solution of
5.19 g (30 mmol) of 4-nitrophthalonitrile[16,40] (1) in 20 mL of dry dimethyl-
formamide (DMF) was added 5.30 g (45 mmol) of 2-ethyl-2-methyl-1,3-propa-
nediol (2) and 10.5 g (75 mmol) of finely ground anhydrous potassium
carbonate. The K_2CO_3 was added in four equal portions at 12 h intervals and
the mixture was stirred at room temperature for a total of 48 h. The
reaction mixture was filtered and washed four times with ethyl acetate. The
filtrate was washed with 300 mL of cold water, brine and dried over mag-
nesium sulfate. The crude product was purified by silica gel column
chromatography (5 x 25 cm) using acetonitrile-benzene (1:19) as eluant which
gave 0.7 g of 1,3-bis-(3,4-dicyanophenyl)-2-ethyl-2-methylpropane (4) mp
157-159 °C (lit.[7] mp 157-158 °C) and 1.5 g of a mixture of 3 and 4 (fraction
2).

Further elution with acetonitrile-benzene (1:9) gave 5.5 g of compound
3. An additional 1.0 g of 3 was isolated by rechromatography of the above
fraction 2. The combined fractions of 3 (6.5 g) were distilled as a clear,
viscous oil to give 6.3 g (86%) of pure 3, bp 195-205 (0.01 Torr, Kugelrohr
apparatus): IR (neat, NaCl) ν_{max} 3450, 3060, 2900, 2240, 1600, 1500, 1250,
840 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.87-7.68 (m, 1H, Ar H-5), 7.31-7.21 (m, 2H, Ar

H-3,6), 3.89 (q, 2H, CH$_2$OAr), 3.55 (q, 2H, CH$_2$OH, J=7 Hz), 1.91 (s, 1H, O-

H), 1.44 (q, 2H, CH$_2$C, J=7 Hz), 0.97 (s, 3H, CH$_3$), 0.89 (t, 3H, CH$_3$CH$_2$, J=7

Hz); ^{13}C NMR (CDCl$_3$) ppm 162.0 (C$_4$), 134.7 (C$_6$), 119.4 (C$_5$), 119.1 (C$_3$),

116.3 (C$_2$), 115.3 + 114.8 (C$_8$, C$_7$), 105.8 (C$_1$), 72.9 (C$_{14}$), 65.3 (C$_9$), 38.5

(C$_{10}$), 25.8 (C$_{12}$), 17.5 (C$_{11}$), 6.3 (C$_{13}$); MS for C$_{14}$H$_{16}$N$_2$O$_2$, m/z (relative

intensity) 244 (M$^+$, 41), 227 (64), 226 (47), 213 (4), 171 (88), 157 (100),

127 (94). Anal. Calcd. for C$_{14}$H$_{16}$N$_2$O$_2$: C, 68.83; H, 6.60; N, 11.47.

Found: C, 68.94; H, 6.77; N, 11.49.

4-(2-Methyl-2-triphenylmethoxybutoxy)benzene-1,2 dicarbonitrile (7) [4-(2-methyl-2-trityloxybutoxy)phthabonitrile].

To a solution of 2.44 g (10 mmol) of **3** in 40 mL of dry pyridine was

added 4.0 g (14 mmol) of freshly prepared trityl chloride (**5**) and the

mixture was stirred at room temperature for 48 h. The pyridine hydro-

chloride was filtered, washed with dry ethyl acetate and the filtrate

evaporated under vacuum at 30-40 $^\circ$C. The oily product was purified on

silica gel using acetonitrile-benzene 1:19 as eluant to give 2 g (83%) of

pure **7**, mp 105-106 $^\circ$C: IR (KBr) ν_{max} 2220, 1600, 1490, 1450, 1300, 1250,

1000, 840 cm^{-1}; ^{1}H NMR δ 7.68-7.06 (m, 18H, Ar), 3.89 (dd, 2H, CH$_2$OAr), 3.05

(q, 2H, CH$_2$OTr, J=7 Hz), 1.52-1.38 (q, 2H, CH$_2$CH$_3$), 0.97 (s, 3H, CH$_3$), 0.77

(t, 3H, CH$_2$CH$_3$, J=6 Hz); ^{13}C NMR (CDCl$_3$) ppm 162.2 (C$_4$), 135.1 (C$_6$), 128.7

(Tr), 127.6 (Tr), 127.0 (Tr), 119.8 (C$_5$), 119.1 (C$_3$), 117.3 (C$_2$), 115.7 +

115.2 (C$_8$, C$_7$), 106.9 (C$_1$), 86.2 (Tr), 72.9 (C$_{14}$), 65.2 (C$_9$), 38.8 (C$_{10}$),

27.0 (C$_{12}$), 18.7 (C$_{11}$), 7.4 (C$_{13}$); MS for C$_{33}$H$_{30}$N$_2$O$_2$, m/z (relative inten-

sity) 486 (M$^+$, 100), 409, 332, 255, 243. Anal. Calcd. for C$_{33}$H$_{30}$N$_2$O$_2$: C,

81.45; H, 6.21; N, 5.75. Found: C, 81.47; H 6.88; N, 5.80.

Polymer-bound 4-(2-methyl-4-triphenylmethoxymethylbutoxy)benzene-1,2-dicarbonitrile (8).

To 12 g (15.6 mmol cl/g) of freshly prepared polymer-bound trityl chloride (6)[17] in 100 mL of dry pyridine-dichloromethane (1:1) was added 10 g (40.9 mmol) of 3 and 0.2 g of 4,4-dimethylaminopyridine[20]. The suspension was stirred at room temperature for 48 h under argon. The polymer was filtered and washed with pyridine, dichloromethane and ethyl acetate to give filtrate A. The polymer was further washed with water, methanol, acetonitrile and ether. The air-dried polymer was extracted in a Soxhlet apparatus with dichloromethane, ethyl acetate and tetrahydrofuran for 5-6 h for each solvent. The polymer was washed with dry ether and air-dried to give 13.5 g of polymer 8: IR (KBr) ν_{max} 2230 cm^{-1}; ^{13}C NMR δ 162.2 (C_4), 134.9 (C_6), 146.0 + 134.0 + 133.0 +128.0 + 127.0 + 125.0 ($C_{polymer}$), 120.2 (C_5), 119.6 (C_3), 117.2 (C_2), 115.2 + 115.0 + (C_8, C_7), 107.0 (C_1), 73.0 (C_{14}), 66.9 (C_9), 38.7 (C_{10}), 26.9 (C_{12}), 18.7 (C_{11}), 8.3 (C_{13}).

From filtrate A, 8.0 g of 3 was recovered. The loading capacity of polymer 8 was determined by cleavage with iodotrimethylsilane[23]. Thus 0.5 g of 8 in 5 mL of dry dichloromethane and 0.2 mL of iodotrimethylsilane was stirred at room temperature for 24 h to yield 65 mg of pure 3, showing polymer 8 to have a loading capacity of 0.53 mmol/g for 3.

1,3-Diiminoisoindolines (9), (10) and (11).

Ammonia was bubbled into a stirred solution of 50 mg of sodium in 50 mL of dry methanol and 0.97 g (2 mmol) of 7 for 1 h at room temperature and 4 h under reflux conditions. Evaporation (with foaming) of the solvent gave 1.04 g of crude 9.

To a solution of 250 mg of sodium in 40 mL of dry methanol and 55 mL of freshly distilled dry tetrahydrofuran (THF) was added 6.0 g of **8**. Ammonia was bubbled into the suspension as above and the polymer was filtered, washed with dry THF and vacuum dried to give 6.0 g of green polymer **10**.

In a similar manner 2.0 g (82 mmol) of **3** reacted with ammonia in a 1:2 mixture of dry methanol and dry THF (33 mL), containing 200 mg of sodium methoxide. The solvent was evaporated to give 2.0 g of the slightly green crude **11**.

In all examples reactions were continued until the crude bis-1,3-diiminoisoindolines did not exhibit nitrile absorptions in the IR spectra. Compounds **9-11** were used in condensation reactions without further purification.

2,9,16-23-Tetra-(2-methyl-2-triphenylmethoxymethylbutoxy)phthalocyanine (12).

A solution of 1.04 g of crude **9** in 8 mL of 2-N,N-dimethylaminoethanol (DME) was heated for 48 h at 160 °C (oil bath) under an argon atmosphere. The dark blue reaction mixture was diluted with water, filtered, washed with water and acetonitrile (until the filtrate was colorless), dried and purified by flash chromatography[32] using toluene as eluant to afford 0.47 g (40%) of a blue shining solid of pure **12**: UV-vis λ_{max} (CH$_2$Cl$_2$) 706 (log ε 5.14), 672 (5.16), 648 (4.85), 608 (4.66), 394 (4.78), 346 nm (5.01); IR (KBr) ν_{max} 3280 (NH), 3040, 2920, 1605, 1490, 1450, 1250, 1010 (NH), 840 cm^{-1}; ^{1}H NMR δ 9.4-8.4 (m), 7.74-7.24 (m), 3.89-3.84 (m), 3.55-3.51 (m), 1.46-1.44 (m), 0.99-0.97 (m), 0.92-0.87 (m), -1.34 (br); MS for C$_{132}$H$_{122}$N$_8$O$_8$, $\underline{m/z}$ (relative intensity) 1949 (M + 1, 13), 1706 (M - Tr, 16), 1464 (M - 2Tr + 1, 19) 1222 (M - 3Tr + 2, 28), 980 (M - 4Tr + 3, 100), 879.

Anal. Calcd. for $C_{132}H_{122}N_8O_8$: C, 81.36; H, 6.31; N, 5.75. Found: C, 81.16; H, 6.49; N, 5.85.

2,9,16,23-Tetra-(2-hydroxymethyl-2-methylbutoxy)phthalocyanine (13).

Condensation of 2.0 g of crude 1,3-bisdiiminoisoindoline **11** in 6 mL of DME under conditions similar to that described for **9**, gave after partial purification by flash chromatography using THF as eluant, a crude product. Further purification on a second column, using hexane-THF 1:3 as eluant, gave 0.78 g (42%) of a dark solid, soluble in dimethyl sulfoxide (DMSO) and pyridine, slightly soluble in methanol and ethanol, and insoluble in toluene, benzene, ether and acetonitrile, as pure **13**: UV-vis λ_{max} (EtOH) 702 (log ε 4.57), 664 (4.64), 638 (4.60), 384 (4.32), 336 nm (4.70); IR (KBr) ν_{max} 3290 (NH), 1610, 1240, 1100, 1010 (NH), 825 cm^{-1}; ^{1}H NMR (pyridine-d_5) δ 8.71-7.02 (br), 6.40 (s), 4.44-4.35 (m), 4.17-4.14 (m), 2.01-1.96 (m), 1.58-1.44 (m), 1.29-1.23 (m), -3.47 (s); ^{13}C NMR (pyridine-d_5) ppm 161.3 (C_4), 147.4 + 137.5 + 127.5 + 125.9 +118.0 + 105.8 + 105.4 (Aromatic C), 72.7 (C_{14}), 66.3 (C_9), 30.8 (C_{10}), 27.4 (C_{12}), 19.3 (C_{11}), 8.5 (C_{13}); MS for $C_{56}H_{66}N_8O_8$, $\underline{m/z}$ (relative intensity) 980 (M + 1, 69), 950 (100), 878 (40), 848 (53), 778 (17). Anal. Calcd. for $C_{56}H_{66}N_8O_8$: C, 68.68; H, 6.79; N, 11.44. Found: C, 68.96; H, 7.19; N, 11.56.

In a different preparation of **13**, 30 mg of pure **12** in 5 mL of dry dichloromethane was stirred with 0.2 mL of iodotrimethylsilane to afford 30 mg of a crude product. Flash chromatography using THF as eluant yielded 20 mg of pure **13**, identical in all respect to **13** prepared above.

2,9,16,23-Tetra-(2-hydroxymethyl-2-methylbutoxy)phthalocyaninatozinc(II) (14).

To 98 mg (0.1 mmol) of **13** in 5 mL of a 1:2 mixture of dry 2-methoxy-ethanol-toluene was added 55 mg (0.2 mmol) of anhydrous zinc acetate. The mixture was stirred at 110-115 °C for 30 h under an argon atmosphere. The total cooled, reaction mixture was applied to a 1 cm diameter flash chromatography column and eluted with ether which removes reactant solvent and impurities. Further elution with freshly distilled THF-hexane 3:2 gave 92 mg (88%) of a dark blue solid (more soluble in organic solvents than **13**) as pure **14**[24]: UV-vis λ_{max} (EtOH) 682 (log ϵ 5.14), 672 (5.10), 616 (4.45), 352 (4.82), 288 nm (4.38); IR (KBr) ν_{max} 1600, 1250, 1100, 1060, 750 cm^{-1}; MS for $C_{56}H_{64}N_8O_8Zn$, $\underline{m/z}$ (relative intensity) 1040, 1041, 1042 (48), 940 (100), 840 (100), 740. Anal. Calcd. for $C_{56}H_{64}N_8O_8Zn$: C, 64.51; H, 6.19; N, 10.75; Zn, 6.27. Found: C, 64.30; H, 6.40; N, 11.00; Zn, 5.79.

Polymer-bound 4-(2-methyl-2-triphenylmethoxymethylbutoxy)phthalocyanine (16).

Using a method previously described for mixed condensations of polymer-bound bis-1,3-diiminoisoindolines[16], a slurry of 2.0 g (1.06 mmol) of **10** and 4.1 g (19 mmol, 6 times excess) of 5-neopentoxy-1,3-diiminoisoindoline[41] (**15**)[7] in 26 mL of a 1:1 mixture of dry DME and DMF was stirred under reflux conditions (bath temperature 160 °C) for 48 h under an argon atmosphere. After the suspension was cooled to room temperature, polymer **16** was filtered, washed twice with DMF, at least ten times with water, methanol, and acetonitrile to afford filtrate A. Further washing with ether, THF, and ether again gave filtrate B. Filtrate B was evaporated to give a dark blue solid. Filtrate A was diluted with a large volume of water and the dark

blue precipitate was filtered, washed with water and acetonitrile and combined with the product for filtrate B. This crude dark blue material was extracted in a Soxhlet extractor with methanol and then with acetonitrile until the filtrates were clear. Purification of the residue by flash chromatography using toluene-hexane 3:1 as eluant gave 2.1 g (52%) of pure 2,9,16,23-tetraneopentoxythalocyanine (17)[7,25] as a dark, blue solid.

The black polymer **16** was extracted in a Soxhlet extractor successively with ether, dichloromethane, toluene and THF until the extract was colorless (ca 3-5 h for each solvent). The black residue was finally washed with anhydrous ether and dried to give 2.2 g of black polymer (**16**).

2,9,16-Tri-(2,2-dimethylpropoxy)-23-(2-hydroxymethyl-2-methyl-butoxy)phthalocyanine[41] (**18**); **2,9-Di-(2,2-dimethylpropoxy)-16,23-(2-hydroxy-methyl-2-methylbutoxy)phthalocyanine**[41] (**20**) + **2,16-Di-(2,2-dimethylpropoxy)-9,23,-(2-hydroxymethyl-2-methylbutoxy)phthalocyanine**[41] (**21**).

A suspension of 1.9 g of polymer **16** in 20 mL of dry, freshly distilled dichloromethane and 0.5 mL of iodotrimethylsilane was stirred for 24 h under argon. The polymer was filtered, washed with dichloromethane and ether, and extracted in a Soxhlet extractor first with toluene and finally with THF until the extracts were clear. A green polymer (1.5 g) was recovered and air-dried. The combined extracts were evaporated to dryness to yield 0.4 g of a green-blue residue, which was washed with water and acetonitrile until colorless. The resulting residue (0.27 g) was dissolved in toluene, pre-absorbed on silica gel and purified by flash chromatography using a 1.5 x 25 cm column. Elution with toluene afforded a trace (3-4 mg) of **17**. Further elution with 2-methoxyethanol-toluene (1:199 to 1:49) gave 170 mg of a middle fraction (B) while continued elution with 2-methoxyethanol-toluene

(3:97 to 1:19) yielded 70 mg of a final fraction (C). Each fraction was analyzed by TLC, UV-vis and mass spectrometry. The mass spectrum of the middle fraction (B) exhibited peaks at an amu of 888 consistent with **18** and a minor peak at 918 consistent with **20** and **21**. Further purification of fraction B by flash chromatography as above gave 162 mg (18% based on **8**) of a dark blue solid of pure **18** (with no contamination with **20** or **21** when analyzed by mass spectroscopy): UV-vis (CH_2Cl_2) λ_{max} 704 (log ε 4.20), 670 (4.67), 656 (4.52), 614 (4.32), 390 (4.47), 342 nm (4.61); IR (KBr) ν_{max} 3200 (NH), 1620, 1250, 1100, 1020 (NH), 750 cm^{-1}; ^{1}H NMR (C_6D_6) δ 8.05-6.98 (m), 4.17-4.01 (m), 3.98-3.57 (m), 3.17-2.97 (m), 1.61 (s), 1.40-1.28 (m), 1.05-0.85 (m), -3.5 to -5.3 (br); MS for $C_{53}H_{60}N_8O_5$, $\underline{m/z}$ (relative intensity) 889 (M + 1, 100) 818 (27), 788 (25). Anal. Calcd. for $C_{53}H_{60}N_8O_5$: C, 71.59; H, 6.80; N, 12.60. Found: C, 71.74; H, 6.99; N, 13.01.

In some instances TLC examination of **18** exhibited 3 closely spaced bands when eluted as follows. To three preparative TLC plates 50 mg of pure **18** was applied and developed 12 times with increasing amounts of 2-methoxy-ethanol-toluene (1:199 to 3:97). Three narrow dark blue bands (R_f = 0.43, 0.37 and 0.25) were observed along with interband streaking. Elution of each band and analysis by mass spectroscopy revealed only **18** for each band. As **18** <u>does</u> exist as a mixture of eight closely related regioisomers, it is likely that they could group themselves into partially separable groups of isomers.

Elution of fraction C by flash chromatography using 2-methoxyethanol-toluene (3:97) as eluant gave 60 mg (6.5% based on **8**) of a dark blue solid of pure **20** and **21**: UV-vis λ_{max} (CH_2Cl_2) 704 (log ε 4.84), 662 (4.84), 656 (4.76), 644 (4.68), 388 (4.61), 342 nm (4.80); IR (KBr) ν_{max} 3400 (br), 3280

(NH), 1610, 1240, 1090, 1015 (NH), 750 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.05-7.00 (m),

4.01-3.75 (v br), 1.58-1.43 (m), 1.31-1.25 (m), 1.17-1.04 (m), -5.57 (br);

MS for $C_{54}H_{62}N_8O_6$, $\underline{m/z}$ (relative intensity) 919 (M + 1, 100), 848 (25), 818

(34), 603 (39), 577 (45), 549 (51). Anal. Calcd. for $C_{54}H_{62}N_8O_6$: C, 70.56;

H, 6.80; N, 12.19. Found: C, 70.47; H, 6.78; N, 12.45.

2-(2,2-Dimethylpropoxy)-9,16,23-tri-(2-hydroxymethyl-2-methyl-butoxy)phthalocyanine[41] (22), (18), (20 and 21), and 13.

From 6.0 g (3.2 mmol) of polymer-bound bis-1,3-diiminoisoindoline 10 and 4.8 g (20 mmol, 2 times excess) of 15 in 50 mL of a 1:1 mixture of DME and DMF was isolated 2.0 g (41%) of pure 17 and 6.5 g of polymer-bound phthalocyanines (16) as described above. A suspension of 5 g of this batch of polymer 16 in 50 mL of 0.3 M HCl in dioxane was stirred at room temperature for 48 h. The polymer was washed as described above to give 4.1 g of cleaved polymer and 0.8 g of a crude phthalocyanine containing product, showing that the polymer had a loading capacity of 0.35 mmol/g. This crude product was purified by the repetitive use of our modified silica gel flash chromatography described herein as for 18 and (20 and 21) described above. As many as 10 columns were required to separate mixed fractions at every stage. Finally, elution with increasing amounts of 2-methoxyethanol-toluene (1:199-1:19) gave in all combined fractions 182 mg (7.7% based on 8 of a pure blue shining phthalocyanine 18, 120 mg (4.9% based on 8) of a mixture of 20 and 21, 10 mg (0.4% based on 8) of pure dark blue 22: UV-vis λ_{max} (CH$_2$Cl$_2$) 702 (log ε 4.61), 672 (464), 648 (4.54), 390 (sh), 340 nm (4.64); MS for $C_{55}H_{64}N_8O_7$, $\blacksquare/z$ (relative intensity) 948 (M$^+$, 68), 860 (100), 758 (13). Anal. Calcd. for $C_{55}H_{64}N_8O_7$: C, 69.59; H, 6.79; N, 11.80. Found: C, 69.57; H, 6.74; N, 11.59.

From the last fractions 10 mg (0.4% based on **8**) of pure **13** was also isolated.

In a solution phase experiment, a mixture of the two crude 1,3-bis-diiminoisoindolines **11** and **15** prepared from 0.78 g (3 mmol) of **3** and 8.3 g (39 mmol) of 4-neopentoxyphthalonitrile[7,25] respectively was condensed in 25 mL of DME as described above for **16** to give 6.5 g of crude product. Extensive chromatography as above eventually afforded 3.1 g (37%) of pure **17**, 1.0 g (38% based on **3**) of pure **18**, 0.12 g (8.2% based on **8**) of **20** and **21**, and mixtures containing **22** and **13**.

2-[2-(3',4'-Dicyanophenoxymethyl)-2-methylbutoxy]-9,16,23-tri(2,2-dimethyl-propoxy)phthalocyanine[41] (23).

As described above for the formation of **3**, 0.40 g (0.45 mmol) of **9**, 0.60 g (3.46 mmol) of **1** in 16 mL of dry DMF and 0.69 g (5 mmol) of anhydrous potassium carbonate (added in six equal portions over five days) was stirred at room temperature for five days. The crude product was purified by flash chromatography. Elution with 400 mL of benzene removed all of the excess **1**. Further elution with acetonitrile-benzene (3:97) gave 0.41 g of a mixture of **23** and starting **18**. Rechromatography of this mixture on a 1.5 x 25 cm column using the same eluant yielded 0.20 g of pure **23** and 0.20 g of a mixture of **23** and **18**. To this latter mixture was added 0.30 g (1.73 mmol) of **1**, and anhydrous K_2CO_3 (10-15 mg) was added every day with stirring during a three week period. Flash chromatography of this product yielded crude **23** which was washed with methanol to remove minor fluorescent impurities. A final flash chromatography yielded 0.17 g of the dark blue shiny **23**, soluble in organic solvents, slightly soluble in acetonitrile and not soluble in alcohols. The reaction yielded in total 0.36 g (79%) of pure

23: UV-vis λ_{max} (CH_2Cl_2) 702 (log ε 5.04), 666 (5.00), 648 (4.80), 606 (4.53), 390 (sh), 350 (4.83); IR (KBr) ν_{max} 3295 (NH), 2240 (CN), 1610, 1240, 1095, 1015 (NH), 750 cm^{-1}; ^{1}H NMR δ 7.75-7.25 (m), 4.21-4.12 (m), 4.01-3.40 (m), 1.98-1.83 (m), 1.33-0.95 (m), -7.72 (br); ^{13}C NMR ppm 162.2 (C_4), 159.31 + 149.4 + 128.9 + 128.2 + 125.3 ($C_{aromatic}$), 135.3 (C_6), 121.0 (C_5), 119.6 (C_3), 117.4 (C_2), 115.6 + 115.2 (C_8, C_7), 107.2 (C_1), 74.4 (C_9), 73.0 (C_{15}), 71.4 (C_{14}), 38.6 (C_{10}), 31.9 (C_{16}), 26.9 (C_{17}), 21.4 (C_{12}), 18.8 (C_{11}), 7.8 (C_{13}); MS for $C_{61}H_{62}N_{10}O_5$, $\underline{m/z}$ 1013 (M-1). Anal. Calcd. for $C_{61}H_{62}N_{10}O_5$: C, 72.16; H, 6.15; N, 13.80. Found: C, 72.18; H, 6.40; N, 13.43.

2-[2-(3',4'-Dicyanophenoxymethyl)-2-methylbutoxy]-9,16,23-tri-(2,2-dimethyl-propoxy)-phthalocyaninatozinc(II)[41] (24).

A mixture of 0.14 g (0.14 mmol) of **23** and 0.10 g (0.55 mmol) of anhydrous zinc acetate in 7 mL of a 2:5 mixture of 2-methoxyethanol-toluene was heated (bath temperature 115 °C) for 2 h. The cooled mixture was applied directly to a normal grade silica gel column and eluted with acetonitrile-benzene (3:97 to 1:99) to give 0.14 g of a crude product. Washing with methanol removed some impurities and flash chromatography on a 1.2 x 15 cm column using acetonitrile-benzene (3:97 to 5:95) gave 0.13 g (90%) of pure **24**: UV-vis λ_{max} (CH_2Cl_2) 684 (log ε 5.36), 674 (5.27), 616 (4.72), 346 nm (5.15), λ_{max} (toluene) 686 (log ε 5.06), 672 (5.00), 614 (4.56), 362 nm (4.85); IR (KBr) ν_{max} 2230 (CN), 1605, 1240, 1100, 1050, 750 cm^{-1}; ^{1}NMR δ 7.70-6.78 (m), 4.85-3.42 (m), 1.61-1.42 (m), 1.22-0.83 (m); ^{13}C NMR ppm 162.2 (C_4), 159.5 + 149.3 + 148.4 + 129.0 + 128.2 + 125.3 ($C_{aromatic}$), 135.2 (C_6), 121.4 (C_5), 119.6 (C_3), 117.4 (C_2), 115.6 + 115.1 (C_8, C_7), 107.2 (C_1), 74.0 (C_9), 73.0 (C_{14}), 71.4 (C_{15}), 38.4 (C_1), 31.9

(C_{16}), 26.9 (C_{17}), 26.4 (C_{12}), 18.8 (C_{11}), 7.8 (C_{13}); MS for $C_{61}H_{60}N_{10}O_5Zn$, m/z 1079, 1078, 1077, 1076 (M^+ cluster). Anal. Calcd. for $C_{61}H_{60}N_{10}O_5Zn$: C, 67.92; H, 5.60; N, 12.98; Zn, 6.06. Found: C, 67.99; H, 5.56; N, 12.25; Zn, 6.53.

In a different experiment, to 0.086 g (0.09 mmol) of **19** and 0.10 g (0.57 mmol) of **1** in 5 mL of dry DMF was added 0.40 g (2.9 mmol) of K_2CO_3 in seven portions over seven days under argon. Flash chromatography as for the isolation of **24** above gave an impure product. Preparative TLC of this crude product and successive elutions with acetonitrile-benzene mixtures (3:97 to 1:9) gave a fast moving spot which after isolation yielded 0.04 g (43%) of very pure **24**, identical to that produced above.

2-[2-(3',4'-Dicyanophenoxymethyl)-2-methylbutoxy]-9,16,23-tri-(2,2-dimethyl-propoxy)phthalocyaninatocopper(II)[41] (25).

A mixture of 0.12 g (0.12 mmol) of **23** and 0.10 g (0.55 mmol) of anhydrous copper acetate was treated as above for **24** to give 0.12 g (94%) of a pure blue solid of 25: UV-vis λ_{max} (CH_2Cl_2) 684 (log ϵ 5.18), 672 (5.01), 614 (4.85), 340 nm (4.94), λ_{max} (toluene) 684 (log ϵ 5.19), 672 (5.10), 612 (4.66), 348 nm (4.82); IR (KBr) ν_{max} 2240 (CN), 1610, 1235, 1090, 750 cm^{-1}; MS for $C_{61}H_{66}N_{10}O_5Cu$, m/z 1077, 1076, 1075 (M^+ cluster). Anal. Calcd. for $C_{61}H_{66}N_{10}O_5Cu$: C, 68.04; H, 5.61; N, 13.00; Cu, 5.90. Found: C, 67.81; H, 5.68; N, 12.80; Cu, 5.48.

1,3-Diiminoisoindolines (26-30).

In a manner similar to that described above for **9-11**, 0.08 g of sodium reacted with 5 mL of methanol to which was added 0.40 (g) (0.4 mmol) of **23** in 40 mL of dioxane and 10 mL of THF to afford 0.4 g of **26**.

Similarly 0.07 g of **24** gave 0.07 g (0.07 mmol) of **27** and 0.47 g (0.43

mmol) of **25** gave 0.47 g of **28**.

Treatment of 1.47 g (8.0 mmol) of commerically available 4-tert-butylphthalonitrile[42] as above for **9** gave 1.47 g of **29**, while treatment of 3.1 g (2.4 mmol) of phthalonitrile in 120 mL of CH_3OH:THF (1:5) gave 3.1 g of **30**. The crude products **26-30** did not exhibit any nitrile absorption in their ir specta and were directly used in subsequent condensations.

1-[2'-(9',16',23',-Tri-(1,1-dimethylethyl)phthalocyaninoxy}]-3-[2'-{9',16',12'-tri-(2,2-dimethylpropoxy)phthalocyaninoxy}]-2-ethyl-2-methylpropane[41,42] (31).

The two crude 1,3-diiminoisoindolines **26**, prepared from 2.0 g (0.2 mmol) of **23**, and **29**, prepared from 1.47 g (8 mmol) of 4-tert-butylphthalonitrile, in 6 mL of DME were heated at 160 °C (oil bath) for 48 h under argon. The dark blue reaction mixture was cooled, poured into water, filtered and washed thoroughly with water and acetonitrile until the filtrate was colorless. The crude product (2.5 g) was dissolved in toluene and pre-absorbed onto normal silica gel for flash chromatography on a 5 x 30 cm column. Elution with hexane-toluene (1:1 to 1:4) yielded 0.65 g (44%) of dark blue 2,9,16,23-tetra-(1,1-dimethylethyl)phthalocyanine[42,43] (**33**). Further elution with toluene and 2-methoxyethanol-toluene (1:199 to 1:49) gave 0.065 g of crude binuclear **31** contaminated with some **33**. This fraction was rechromatographed using a 3:197 mixture of 2-methoxyethanol-toluene as eluant to provide upon evaporation 0.03 g (9%) of a blue, shiny solid, very soluble in organic solvents, of pure **31**: UV-vis λ_{max} (CH_2Cl_2) 638 (log ϵ 5.01) 338 nm (5.07), λ_{max} (toluene) 638 (log ϵ 5.01), 340 nm (5.04); IR (KBr) ν_{max} 3300 (NH), 1615, 1240, 1100, 1015 (NH), 750 cm^{-1}; ^{1}H NMR δ 9.57-9.50 (m), 8.90-7.99 (br), 7.82-7.38 (m), 4.28-3.53 (m), 1.82-1.46 (m), 1.45

(s), 1.44 (s), 1.43-1.23 (m), 0.95-0.91 (m), -4.44 to -6.5 (br); MS for

$C_{97}H_{100}N_{16}O_5$, $\underline{m/z}$ 1571.8, 1570.8, 1569.8, 1568.8 (M^+ cluster). Anal. Calcd.

for $C_{97}H_{100}N_{16}O_5$: C, 74.20; H, 6.42; N, 14.27. Found: C, 74.34; H, 6.52;

N, 13.54.

1-[2'-{9',16',23'-Tri-(1,1-dimethylethyl)phthalocyaninoxy}]-2-ethyl-2-methyl-3-(2-phthalocyaninoxy)propane[42] (32).

The two crude 1,3-diiminoisoindolines **26**, prepared from 2.0 g (0.2

mmol) of **23**, and **30**, prepared from 3.1 g (2.4 mmol) of phthalonitrile in 12

mL of DME were heated at 160 °C for 60 h under an argon atmosphere. The

reaction mixture was diluted with water, filtered, washed thoroughly with

water and dried. Exhaustive extraction of the blue solid in a Soxhlet

extractor, first with methanol and then acetonitrile, removed many im-

purities but left the insoluble phthalocyanine **34** and the binuclear phthalo-

cyanine **32** in the residue. Further extraction using dichloromethane and

then THF dissolved binuclear **32** in the filtrate leaving the insoluble **34** in

the thimble. Evaporation of the filtrate gave 20 mg of crude binuclear **32**.

Flash chromatography of this product on a short 1 x 3 cm column using

dichloromethane and finally THF as eluants gave 5 mg (2%) of pure dark blue

32: UV-vis λ_{max} (CH_2Cl_2) 692 (log ϵ 4.71), 656 (4.68), 638 (4.34), 600

(4.12), 338 nm (4.52), λ_{max} (THF) 692 (log ϵ 4.92), 656 (4.94), 636 (4.57),

596 (4.35), 338 nm (4.75); MS, exact mass calcd. for $C_{85}H_{76}N_{16}O_5$, $\underline{m/z}$

1400.6183, obsd. $\underline{m/z}$ 1400.62.

1,3-Bis-[2'-{9',16',23'-tri-(2,2-dimethylpropoxy)phthalocyaninoxy}]-2-ethyl-2-methylpropane[41] (35) via (27).

Two crude 1,3-diiminoisoindolines **15** and **27**, prepared from 0.5 g (2.3 mmol) of 4-neopentoxyphthalonitrile[7] and 0.07 g (0.07 mmol) of **24** were heated in 5 mL of DME at 160 °C (oil bath) for 48 h under argon. The resulting mixture was worked up as described below for **32**. The crude product (0.28 g) was separated by flash chromatography, to give 0.08 g (17%) of pure **17** using hexane-toluene (1:1) as eluant, followed by 0.0058 g (1%) of **36**, and 10 mg (9%) of **32** (MS of **32** identical with MS of **32** previously described).

1,3-Bis-[2-{9',16',23'-tri-(2,2-dimethylpropoxy)phthalocyaninoxy}]-2-ethyl-2-methylpropane Monocopper(II)[41] (37).

Two crude 1,3-diiminoisoindolines **15** and **28**, prepared from 2.8 g (13 mmol) of 4-neopentoxyphthalonitrile[7] and 0.47 g (0.43 mmol) of **25** respectively, were treated as for the preparation of **35** above. The dark blue reaction mixture was cooled, poured into water, filtered and washed thoroughly with water and acetonitrile until the filtrate was colorless. The crude, dried product (1.5 g) was dissolved in toluene and preabsorbed onto silica gel for flash chromotography on a 5 x 30 cm column. Elution with hexane-toluene (1:2) gave 1.04 g (37%) of pure **17**. Further elution with hexane-toluene (1:3, 1:4), toluene, and a 1:199 mixture of 2-methoxy-ethanol-toluene gave 0.12 g of a mixture of **17** and **31**. Finally, elution with 2-methoxyethanol-toluene (1:99, 1:4) gave 0.25 g of a dark blue fraction of higher molecular weight phthalocyanines and impurities which were not further investigated. The mixed monomer-dimer fraction were rechromatography using hexane-toluene (1:4) and toluene as eluants to

provide 0.03 g (12%) of a dark blue shining solid of pure **37**: UV-vis λ_{max} (CH$_2$Cl$_2$) 672 (log ϵ 4.87), 638 (4.91), 336 nm (4.98), λ_{max} (toluene) 704 sh, 674 (log ϵ 4.99), 638 (5.01), 400 sh, 340 nm (5.05); IR (KBr) ν_{max} 3310 (w, NH), 1620, 1245, 1100, 1070, 1020 (s, NH) cm^{-1}; MS for C$_{100}$H$_{104}$N$_{16}$O$_8$Cu, m/z (relative intensity) 1723.75 + 1722.75 + 1721.75 (100) + 1720.75 + 1719.75 (M$^+$ cluster). Anal. Calcd. for C$_{100}$H$_{104}$N$_{16}$O$_8$Cu: C, 69.72; H, 6.08; N, 13.01; Cu, 3.69. Found: C, 70.02; H, 6.21; N, 12.87; Cu, 3.50.

2,9,16,23-Tetra-[2-(3',4'-dicyanophenoxymethyl)-2-methyl-butoxy]phthalocyanine (38).

To a mixture of 0.52 g (0.5 mmol) of **13** and 1.8 g (10.5 mmol) of **2** in 15 mL of dry DMF was added 3.0 g (21 mmol) of finely ground anhydrous potassium carbonate in 0.2 g portions every 12 h over 7 days with vigorous stirring. The reaction mixture was filtered and washed four times with 50 mL of ethyl acetate. The filtrate was washed with 300 mL of water, dried over MgSO$_4$, filtered and evaporated to dryness. Extraction of the residue with ether in a Soxhlet apparatus for 6 h removed the excess **2**. Flash chromatography of the remaining blue residue using ethyl acetate-THF (4:1) or hexane-THF (2:3) as eluant gave a blue product **38** which was very soluble in acetronitrile, THF and ethyl acetate; moderately soluble in dichloro-methane and insoluble in ether, benzene, toluene, and methanol. Thus, chromatography yielded 0.68 g (87%) of pure **38**: UV-vis λ_{max} (CH$_2$Cl$_2$) 720 (log ϵ 4.64), 668 (4.57), 644 (4.22), 608 (4.13), 486 sh (3.75), 344 nm (4.45); IR (KBr) ν_{max} 3300 (NH), 2240 (CN), 1600, 1260, 1105, 1020 (NH), 840 cm^{-1}; ^{1}H NMR δ 9.42-8.79 (br), 7.57-7.04 (br), 4.14-3.91 (m), 1.65-1.49 (m), 1.27-0.87 (m), -1.04 (br); ^{13}C NMR ppm 162.4 (C$_4$), 135.3 (C$_6$), 119.6 (C$_3$, C$_5$), 117.6 (C$_2$), 115.6 + 115.2 (C$_8$, C$_7$), 105.5 (C$_1$), 65.3 (C$_9$), 38.7 (C$_{10}$),

27.1 (C_{12}), 19.0 (C_{11}), 8.0 (C_{13}); MS for $C_{88}H_{74}N_{16}O_8$, $\underline{m/z}$ (relative

intensity) 1484 (54), 1483 (M + 1, 100), 1482 (93), 1256 (62), 1128 (4),

1029 (15). Anal. Calcd. for $C_{88}H_{74}N_{16}O$: C, 71.23; H, 5.02; N, 15.10.

Found: C, 71.22; H, 5.28; N, 15.37.

2,9,16,23-Tetra-[2-(3',4'-dicyanophenoxymethyl)-2-methyl-

butoxy]phthalocyaninatozinc(II) (39).

A mixture of 0.20 g (0.13 mmol) of **38** and 0.10 g (0.5 mmol) of an-

hydrous zinc acetate in 70 mL of a 2:5 mixture of 2-methoxyethanol-toluene

was heated at 115 °C for 2 h under an argon atmosphere. Flash chromatog-

raphy of the crude reaction mixture using acetonitrile-benzene (1:19) as

eluant gave 0.16 g (78%) of pure **39**: UV-vis λ_{max} (CH_2Cl_2) 686 (log ε 5.13),

672 (5.00), 614 (4.63), 346 nm (4.91); IR (KBr) ν_{max} 2245 (CN), 1600, 1480,

1255, 1100, 1060, 840 cm^{-1}; MS for $C_{88}H_{72}N_{16}O_8Zn$, $\underline{m/z}$ 1549, 1548, 1547 (M$^+$,

100), 1546.5, 1545.5, 1544.6, 1421, 1321, 1194, 1094. Anal. Calcd. for

$C_{88}H_{72}N_{16}O_8Zn$: C, 68.32; H, 4.69; N, 14.49; Zn, 4.22. Found: C, 67.85; H,

4.98; N, 14.02; Zn, 4.80.

2,9,16,23-Tetra-[2-(3',4'-dicyanophenoxymethyl)-2-methyl-

butoxy]phthalocyaninatocopper(II) (40).

Similarly, 0.15 g (0.10 mmol) of **38** and 0.18 (g) (1 mmol) of anhydrous

copper acetate gave a crude product which was chromatographed on silica gel

using freshly distilled THF. Further purification on a silica gel column by

elution with acetonitrile-benzene (1:9) gave 0.1 g (65%) of a THF and aceto-

nitrile soluble blue product **40**. UV-vis λ_{max} (CH_2Cl_2) 682 (log ε 5.01), 674

(4.93), 614 (4.41), 364 (4.25), 340 nm (4.62); IR (KBr) ν_{max} 2240 (CN),

1600, 1250, 1100, 1080, 750 cm^{-1}; MS for $C_{88}H_{72}N_{16}O_8$ Cu, $\underline{m/z}$ (relative

intensity) 1546.5 (65), 1545.5 (100), 1544.5 (100), 1543.5 (64), 1402, 1320,

1091. Anal. Calcd. for $C_{88}H_{72}N_{16}O_8$ Cu: C, 68.39; H, 4.69; N, 14.90; Cu, 4.11. Found: C, 68.17; H, 5.50; N, 14.57; Cu, 3.74.

Tetrakis-1,3-Diiminoisoindolines (41), (42) and (43).

As previously described for **26-28**, 0.15 g (1 mmol) of **38** was added to 10 mL of a 1:2 mixture of methanol-THF to which 0.1 g of sodium had been added. Ammonia was bubbled into the solution for 1 h at room temperature and for 4 h under reflux conditions. Evaporation of the solvent gave 0.15 g of crude **41** which was used directly in the next step. Similarly, 0.07 g (0.04 mmol) of **39** gave crude **42**. Both **41** and **42** were slightly soluble in methanol and hot DME. A similar reaction on 0.15 g (0.1 mmol) of **40** gave a precipitate of **43** which was insoluble in the above solvents. Infrared spectra of **41-43** did not show the presence unreacted **38-40**.

2,9,16,23-Tetra-[2-{23'-{2',9',16'-tri-(2,2-dimethylpropoxy)phthalocyani-noxymethyl}-2-methylbutoxy}]phthalocyanine[41] (44).

The two crude 1,3-bisdiiminoisoindolines **41** and **15**, prepared from 0.11 g (0.08 mmol) of **38** and 0.65 g (3 mmol) of 4-neopentoxyphthalonitrile[7,25] were dissolved in 10 mL of DME and heated at 160 °C for 48 h under argon. The dark blue residue was diluted with water, filtered and washed with water, acetonitrile and methanol. Flash chromatography of 0.5 g of dry crude material using hexane-toluene (1:1 to 1:4) and toluene as eluants gave 0.29 g (45%) of pure **17**. Further elution with 2-methoxyethanol-toluene (1:199 to 1:9) yielded 0.07 g of a mixture of **17** and **44**. Continued elution with THF gave 0.06 g of more **44** containing fluorescent and green impurities. Some of these impurities were removed by extraction with acetonitrile. Rechromatography of these last two fractions on a 5 x 50 cm gel permeation chromatography column[9,44], packed with Bio-Beads SX1, 200-450 mesh, yielded

a front running pentanuclear phthalocyanine fraction. Further flash chromatography of this band on a short column using freshly distilled THF as solvent gave 0.04 g (12%) of pure **44**: UV-vis λ_{max} (CH_2Cl_2) 698 sh (log ε 4.64), 662 sh (4.73), 636 (4.78), 336 nm (4.81); IR (KBr) ν_{max} 3280 (NH), 1600, 1250, 1080, 1010 (NH), 790, 750 cm^{-1}; MS for $C_{244}H_{250}N_{40}O_{20}$, m/z 4062. Anal. Calcd. for $C_{244}H_{250}N_{40}O_{20}$: C, 72.13; H, 6.20; N, 13.79. Found: C, 72.04; H, 6.23; N, 13.72.

Modifications to the Flash Chromatography[32,33] Procedure.

The column was prepared with a small plug of glass wool in the bottom of the column overlaid by a short layer of sand and flash chromatography grade silica gel as previously described. The bottom stopcock was opened and connected to a vacuum pump and evacuated for at least five minutes before solvent is added to the column. Solvent is added under vacuum until the solvent reaches the bottom of the silica gel at which time the stopcock was closed. The column was allowed to equilibrate for a minimum of seven minutes at which time the solvent fully wetted all the silica gel. The compounds or mixture to be separated were dissolved in an appropriate solvent and preabsorbed on normal grade silica gel and applied to the top of the column. Forced elution with nitrogen on argon as before[32,33] effected excellent separations.

Acknowledgement.

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CN

O_2N — [benzene ring] — CN

1

+

$HOCH_2 - \underset{\underset{CH_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_2OH$

2

$\xrightarrow[\text{DMF}]{K_2CO_3}$

$ROCH_2 - \underset{\underset{CH_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_2O$ — [benzene ring] — CN, CN

3 R = H

4 R = [benzene ring with CN, CN]

CN 7

1 2 8 CN

6   3

5   4

11 CH3

ROCH$_2$—C—CH$_2$O
14 | 13
10   9   CH$_2$CH$_3$
         12

3 + RCl

(CH$_3$)$_3$SiI

5 R = Tr,   6 R = ⓟ—Tr

7 R = Tr

8 R = ⓟ—Tr

NH$_3$,
CH$_3$ONa

NH$_3$,
CH$_3$ONa

NH   NH   NH

CH$_3$
|
ROCH$_2$—C—CH$_2$O
|
CH$_2$CH$_3$

9 R = Tr,   10 R = ⓟ—Tr

NH   NH   NH

CH$_3$
|
HOCH$_2$—C—CH$_2$O
|
CH$_2$CH$_3$

11

9

11

1) (CH₃)₃SiI
2) M(OAc)₂

12   R = CH₂C–CH₂OTr
            |
            CH₃
            |
            CH₂CH₃

13   R = CH₂C–CH₂OH, M = H₂
            |
            CH₃
            |
            CH₂CH₃

14   R = CH₂–C–CH₂OH, M = Zn
              |
              CH₃
              |
              CH₂CH₃

10

+

11

15   R = OCH₂C(CH₃)₃

$\xrightarrow[\;2)\;M(OAc)_2\;]{\;1)\;H^+\;}$ $\triangle$

+ 17

16   R = CH₂–C(CH₃)(CH₂CH₃)–CH₂OTr, R₁ = R₂ = R₃ = CH₂C(CH₃)₃, M = H₂

17   R = R₁ = R₂ = R₃ = CH₂C(CH₃)₃, M = H₂

18   R = CH₂–C(CH₃)(CH₂CH₃)–CH₂OH, R₁ = R₂ = R₃ = CH₂C(CH₃)₃, M = H₂

19   R = CH₂–C(CH₃)(CH₂CH₃)–CH₂OH, R₁ = R₂ = R₃ = CH₂C(CH₃)₃, M = Zn

20   R = R₁ = CH₂–C(CH₃)(CH₂CH₃)–CH₂OH, R₂ = R₃ = CH₂C(CH₃)₃, M = H₂

21   R = R₂ = CH₂–C(CH₃)(CH₂CH₃)–CH₂OH, R₁ = R₃ = CH₂C(CH₃)₃, M = H₂

22   R = R₁ = R₂ = CH₂–C(CH₃)(CH₂CH₃)–CH₂OH, R₃ = CH₂C(CH₃)₃, M = H₂

13   R = R₁ = R₂ = R₃ = CH₂–C(CH₃)(CH₂CH₃)–CH₂OH,

26 R = CH₂C(CH₃)₃, M = H₂

27 R = CH₂C(CH₃)₃, M = Zn

28 R = CH₂C(CH₃)₃, M = Cu
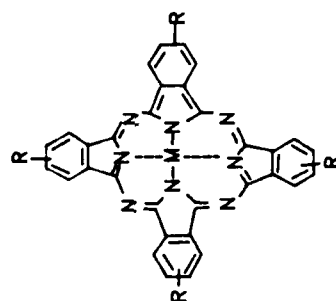
33 R = C(CH₃)₃, M = H₂

34 R = H, M = H₂

17 R = OCH₂C(CH₃)₃, M = H₂

36 R = OCH₂C(CH₃)₃, M = Zn

+
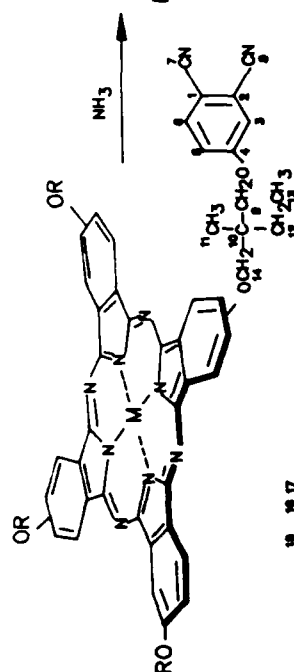
23 R = CH₂C(CH₃)₃, M = H₂

24 R = CH₂C(CH₃)₃, M = Zn

25 R = CH₂C(CH₃)₃, M = Cu
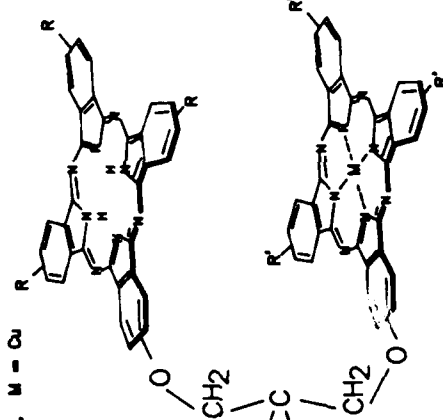
31 R = OCH₂C(CH₃)₃, R' = C(CH₃)₃, M = H₂

32 R = OCH₂C(CH₃)₃, R' = H, M = H₂

35 R = R' = OCH₂C(CH₃)₃, M = H₂

37 R = R' = OCH₂C(CH₃)₃, M = Cu
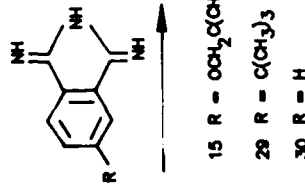
15 R = OCH₂C(CH₃)₃

29 R = C(CH₃)₃

30 R = H

NH₃

1) K₂CO₃
2) M(OAc)₂

18
OR
19

13 + [structure with CN, O₂N, CN] → 1) K₂CO₃ / 2) NH₃

2

15

17 +

38 R = CH₂—C(CH₃)(CH₂CH₃)(CH₂CH₃)—CH₂O— , M = H₂

39 R = CH₂—C(CH₃)(CH₂CH₃)—CH₂O— , M = Zn

40 R = CH₂—C(CH₃)(CH₂CH₃)—CH₂O— , M = Cu

41 R = CH₂—C(CH₃)(CH₂CH₃)—CH₂O— , M = H₂

42 R = CH₂—C(CH₃)(CH₂CH₃)—CH₂O— , M = Zn

43 R = CH₂—C(CH₃)(CH₂CH₃)—CH₂O— , M = Cu

R" = CH₂—C(CH₃)(CH₂CH₃)—CH₂O—

44 R' = CH₂C(CH₃)₃